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INDIRECT MEASUREMENT OF THE VISCOSITY OF THE INTERGRANULAR
GLASS PHASE IN YTTRIA-SINTERED SILICON NITRIDE

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ABSTRACT

Dense, sintered Si_3N_4 possesses a residual intergranular glass phase which softens at high temperatures, resulting in degradation of the ceramic's mechanical properties at these temperatures. An important parameter in the determination of the high temperature mechanical properties of sintered Si_3N_4 is the temperature-viscosity relationship of the intergranular glass. In this paper, a method for indirectly measuring the intergranular glass viscosity at a given temperature using physical modelling of a two-phase glass crystal microstructure and beam-bending viscometry measurements of Si_3N_4 is described. Intergranular glass viscosities obtained by this method are presented for a yttria-sintered Si_3N_4 .

INTRODUCTION

Si_3N_4 is a material that has received considerable interest in recent years for use in structural components for high temperature applications, in particular the all-ceramic gas turbine engine. Because of its low self-diffusivity up to its decomposition temperature, Si_3N_4 requires the use of a sintering aid, commonly a metal oxide, for fabrication of fully dense materials. As a result of this processing, a residual glass phase is present at the grain boundaries [1, 2]. At high temperatures, the degradation of mechanical properties, such as flexural strength and creep resistance, has been attributed to the softening of this intergranular glass phase [3]. In a number of investigations, it has been presumed that the temperature-viscosity relationship of the intergranular glass has a direct influence on the mechanical properties above the glass softening point [4, 5]. It has been suggested that improvements in the high temperature mechanical properties can be obtained by either increasing the viscosity of the intergranular glass through suitable compositional changes [6] or by reducing the volume fraction of glass phase present through crystallization heat treatments [7]. Although it has been demonstrated that reduced glass volume fractions do enhance the high temperature mechanical properties [8], it has also been shown that the existence of a very thin amorphous phase may always be present due to thermodynamic constraints [9]. Hence, the physical properties of the glassy phase, in particular the viscosity, may be a limiting factor in the optimization of the high

temperature mechanical properties. Knowledge of the intergranular glass viscosity at a given temperature, along with the appropriate mathematical models, can be useful in the prediction of creep rates, flexural strengths, and times to failure. Therefore, the purpose of the present study is to obtain the viscosity of the intergranular glass phase as a function of temperature in yttria-sintered Si_3N_4 . To accomplish this, physical modelling of a two phase glass/crystal microstructure, coupled with beam bending viscometry measurements of the apparent viscosities of the sintered silicon nitride at various temperatures, were performed.

EXPERIMENTAL PROCEDURES

Direct measurements of the true viscosity of the intergranular glass in dense yttria-sintered Si_3N_4 are not possible due to the polyphase microstructure of dense Si_3N_4 . Any viscosity measurements performed on bulk Si_3N_4 samples will produce an apparent viscosity value, resulting from the viscosity of the parent yttrium-silicate glass and the effect on that viscosity due to the presence of $\beta\text{-Si}_3\text{N}_4$ crystals within the glass. In addition, it is not possible to perform direct viscosity measurements on bulk glass with compositions similar to the intergranular glass in yttria-sintered Si_3N_4 . These glasses will devitrify upon cooling from the melt [10]. Hence, in order to obtain values for the true viscosity of the intergranular glass in yttria-sintered Si_3N_4 , an indirect measurement approach is required. Basically, this approach involves the physical modelling of a two-phase microstructure by fabricating glass/crystal composites containing a parent glass of known temperature-viscosity relationship and crystalline material of known specific volume. The volume fraction of crystalline material is varied in these composites and the effect upon the viscosity of the parent glass is noted as a function of volume fraction crystalline content. A curve is then constructed which relates the volume fraction of crystalline content in the composites to the relative viscosity, η_{rel} , defined as the ratio of the measured composite viscosity to the true glass viscosity at a given temperature. Using values of the relative viscosity obtained from this curve, combined with measurements of the apparent viscosity in the bulk Si_3N_4 , allow the calculation of the true intergranular glass viscosity.

In this study, four different bulk Si_3N_4 compositions were processed. The compositions and sintering conditions are listed in Table 1. Greater than 98% theoretical density was achieved for these compositions, with the exception of the SN60/40, which attained 95% density. The 6Y and SN60/40 were processed so that the intergranular glass phase was silica rich, with a $\text{SiO}_2 : \text{Y}_2\text{O}_3$ molar ratio of $\approx 3.5 : 1$ in the starting powders. The SN84/16 and SN76/24 were processed with a $\text{SiO}_2 : \text{Y}_2\text{O}_3$ ratio of $2 : 1$ in the starting powders. The powder processing and sintering of the green bodies was performed at NASA Lewis Research Center, Cleveland, OH. Details of the processing have been published previously [11]. X-ray diffraction (XRD) of the as-sintered bars was performed both before and after viscosity measurements to check for devitrification of the glass phase. SEM of etched microstructures was performed on each composition and determinations of the glass volume fractions were made using a Zeiss videoplan image analyzer.

The physical modelling was accomplished by fabricating a series of fully dense, hot-pressed composites containing -325 mesh Al_2O_3 and Corning 7761 glass. The volume fractions of Al_2O_3 in the composites were 30, 40, and 50 vol%. The pressing

conditions were at 870 °C and 1000 - 2000 psi for 15 minutes. XRD was performed on each of the composites before and after viscosity measurements to check for devitrification of the glass phase.

Compositions and Sintering Conditions for Si ₃ N ₄				
Composition	Mill charge (wt%)			Sintering Conditions
	Si ₃ N ₄	Y ₂ O ₃	SiO ₂	
6Y	86.52	6.77	6.71	2140 C, 4 hr, 5 MPa N ₂
SN84/16	86.47	8.83	4.70	2140 C, 2 hr, 5 MPa N ₂
SN76/24	79.40	13.45	7.15	2140 C, 4 hr, 5 MPa N ₂
SN60/40	59.37	21.25	19.38	1900 C, 8 hr, 2.5 MPa N ₂

Table 1. Processing and sintering conditions for Si₃N₄.

Viscosity measurements were made using the beam-bending technique as described by Hagy [12]. In this technique, the rate of deflection of a centrally loaded beam in a three-point loading configuration is measured and related to the viscosity by the equation

$$\eta = \frac{gL^3}{2.4I_c v} \left[M + \frac{\rho AL}{1.6} \right], \quad (1)$$

where η = viscosity (poise), g = 980 cm/sec², L = span length, cm, I_c = cross sectional moment of inertia, cm⁴, v = midpoint deflection rate, cm/min, M = applied load, grams, ρ = specimen density, g/cc, and A = cross-sectional area of test beam, cm². In this study, two separate viscometers were employed: for the bulk Si₃N₄ materials, a top loading configuration was used, wherein loads were applied via a SiC

loading rod and deformation of the specimen was detected by a LVDT coupled to the rod. This construction was necessary because of the higher loads required to obtain measurable deformation rates for these materials. The deflection of the specimen was then plotted versus time on a chart recorder. After making necessary corrections to the data to account for transient differential thermal expansion within the apparatus, equation (1) was applied to the deflection data. The other viscometer, which was used with the composites, utilized a .100 inch diameter sapphire rod to load the specimens from the bottom. In either case, the underlying principle of operation was identical. The error in the measured viscosity for either viscometer was $\pm 10\%$, and the error in temperature measurement was $\pm 1.5^\circ\text{C}$. The accuracy of the viscometers was ascertained by checking them against viscosity data for fused silica [13] and National Institute of Standards standard reference material SRM 711 viscosity standard.

RESULTS

SEM and volume fraction determinations

The typical etched microstructures of the sintered Si_3N_4 is shown in figure 1. The microstructures of each composition are basically the same, consisting of elongated, hexagonal, interlocking $\beta\text{-Si}_3\text{N}_4$ crystals. The microstructures were very uniform over the entirety of each sample. The dark regions are the areas where the grain boundary glass has been etched out by the HF acid treatment.

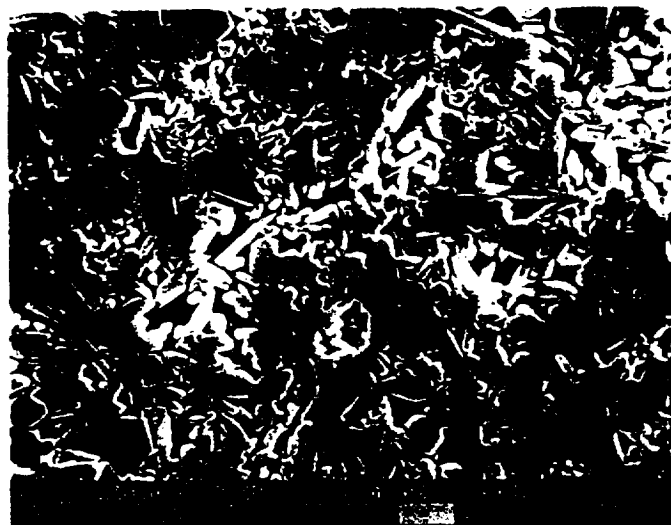


Figure 1. Microstructure of SN84/16 sintered silicon nitride.

To obtain the volume fraction of glass phase present in a given material, the area fraction occupied by the $\beta\text{-Si}_3\text{N}_4$ grains in an etched microstructure was determined and this value subtracted from unity to obtain the area fraction occupied by the glass. The principle of equivalence of area and volume fractions was then employed to obtain the volume fraction of glass phase present. The average measured values, calculated from three micrographs from each composition, were 16.3 ± 3.0 ,

22.3 ± 2.1 , 17.3 ± 3.2 , and 23.0 ± 1.7 vol% for the 6Y, SN84/16, SN76/24, and SN60/40 compositions respectively.

Composite bar modeling

The curve relating volume fraction of Al_2O_3 in the composites to the average relative viscosity $\eta_{\text{rel,avg}}$ was prepared from the composite bar viscosity data. A second degree polynomial curve fit was applied to the data, resulting in the following relation for $\eta_{\text{rel,avg}}$:

$$\log_{10} \eta_{\text{rel,avg}} = -1.6381 \cdot 10^{-2} + 3.9309V + 5.66768V^2, \quad (2)$$

where V = the volume fraction of Al_2O_3 . This curve is shown in figure 2.

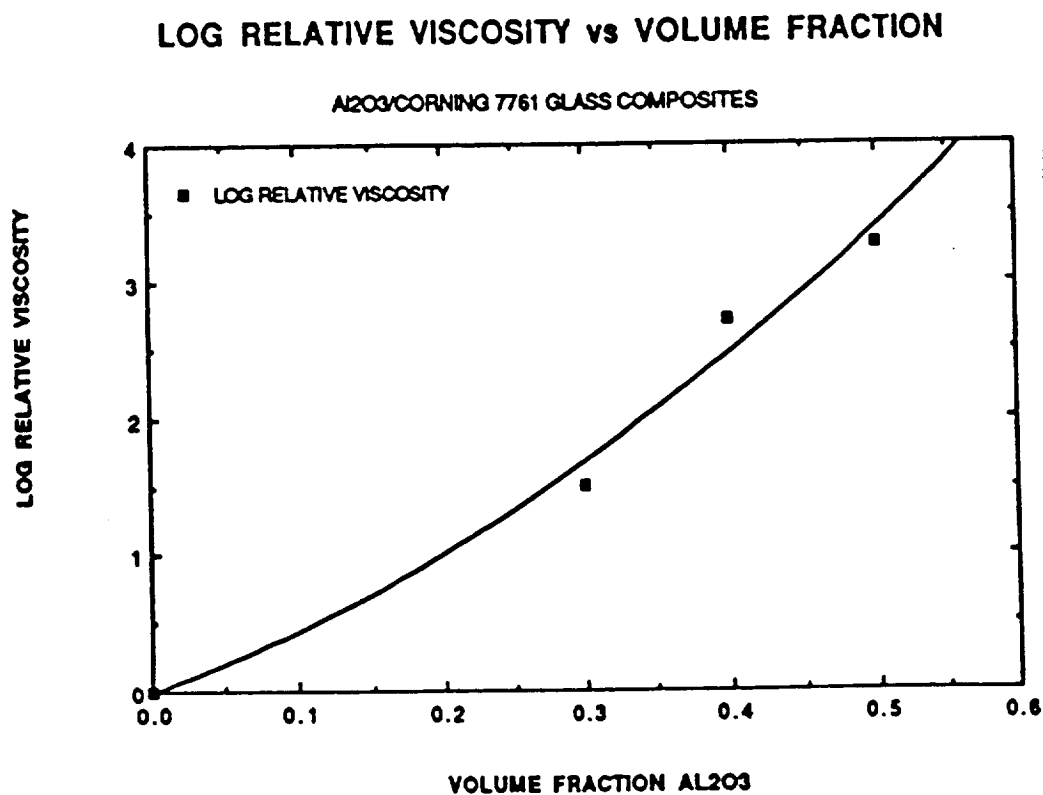


Figure 2. Volume fraction Al_2O_3 vs $\log_{10} \eta_{\text{rel,avg}}$

Viscometry of bulk Si_3N_4

All of the corrected deflection vs time curves exhibited two characteristic stages of deformation which are manifested in the slopes of the curves. The first stage, occurring upon the instant of loading, is a region of initial rapid deflection rate which quickly diminishes with time. The second stage is a region of constant deflection rate. A typical curve is shown in figure 3. These curves are structurally similar to creep curves (strain vs time) for similar Si_3N_4 materials [14], as well as the creep curves for other ceramics containing an intergranular glass phase. In this study, the deflection rates corresponding to the constant deflection rate region of the deflection curves were calculated by performing a least-squares fit to the data over this portion. The apparent viscosities of the bulk Si_3N_4 compositions, calculated by applying equation (1) to the deflection rate data, are listed in table 2. In this table, N/A indicates that a viscosity could not be calculated from the data. Also listed in this table are the calculated intergranular viscosities for each listed apparent viscosity value. These values are calculated on the basis of relative viscosity factors obtained from equation (2).

SN76 #6, 1355 C, 281 MPa

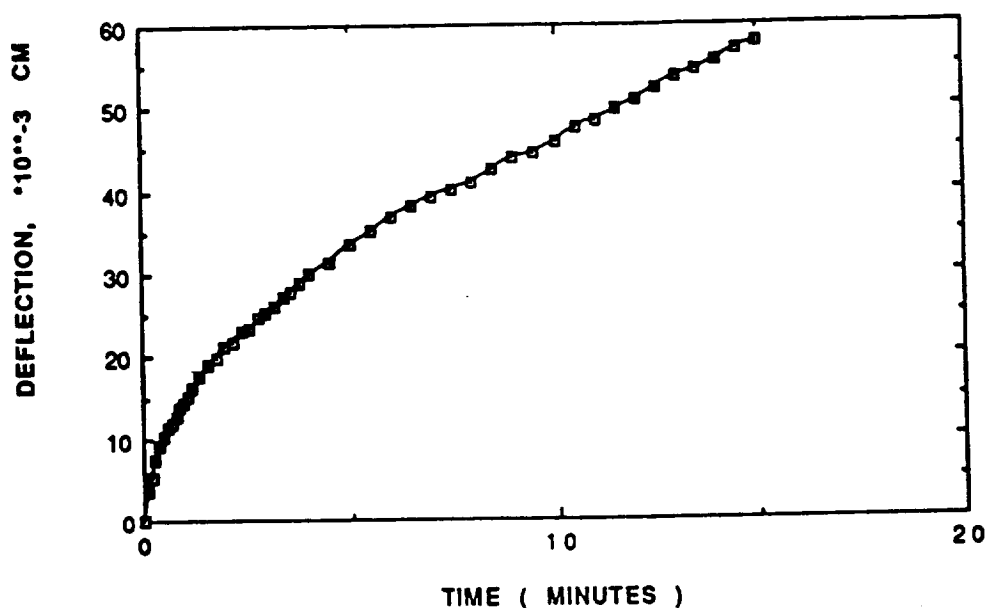


Figure 3. Typical deflection-time curve of sintered silicon nitride

DISCUSSION

The apparent viscosity data is seen to decrease with increasing temperature as expected. For example, the apparent viscosity of SN84/16 decreases from $14.73 \log_{10} \text{ Pa s}$ to $13.34 \log_{10} \text{ Pa s}$ as the temperature increases from 1305°C to 1405°C .

Summary of sintered Si_3N_4 viscosity data.			
composition	T (°C)	$\log_{10} \eta_{\text{app}} (\log_{10} \text{ Pa s })$	$\log_{10} \eta_{\text{int}} (\log_{10} \text{ Pa s })$
6Y(K) #2	1305	N/A	N/A
#5	1330	14.45	7.20 [6.79-7.60]
#3	1355	13.96	6.71 [6.30-7.11]
#6	1405	N/A	N/A
SN84/16 #21	1305	14.73	8.27 [7.99-8.53]
#16	1355	13.79	7.33 [7.05-7.59]
#8	1405	13.34	6.88 [6.60-7.14]
SN76/24 #12	1305	13.66	6.54 [6.11-6.96]
#7	1330	13.62	6.50 [6.07-6.92]
#6	1355	13.40	6.28 [5.85-6.70]
#11	1385	14.01	6.89 [6.46-7.31]
#4	1405	14.40	7.28 [6.85-7.70]
SN60/40 #8	1305	13.83	7.45 [7.24-7.67]
#9	1330	13.98	7.60 [7.39-7.82]
#5	1355	N/A	N/A
#7	1405	N/A	N/A

Table 2. Summary of sintered silicon nitride viscosity data.

Exceptions to this in the viscosity data occur in the SN76/24 and 6Y above 1385 °C and in the SN60/40. The expected decrease in apparent viscosity is observed in the SN76/24 material until 1385 °C is reached, whereupon the apparent viscosity is seen to increase sharply. This is due to crystallization of the glassy phase, thereby increasing the total amount of crystallinity in the material. From equation (2), it is clear that increased crystallinity results in higher values of η_{relLvg} , and therefore increased apparent viscosities. Crystallization of the intergranular glass was observed to occur to some extent during all of the tests. No attempt was made to obtain an estimate of the amount of crystallization. Measurements of the apparent viscosity were made 15 minutes after the furnace reached the desired setpoint. This was done in order to try to minimize the effects of crystallization to the viscosity measurements. Additionally, there is no microstructural evidence to suggest that dissolution of the β - Si_3N_4 into the glass phase occurred.

Average values of the intergranular glass viscosity based on the measured volume fraction were calculated for 1305, 1330, and 1355 °C. These values are plotted vs $1/T$ in figure 4 along with data obtained for Amersil fused silica. The viscosity of the intergranular glass is seen to be ≈ 3 orders of magnitude less than that of fused silica at a given temperature within the range of study. This is as expected, since pure silica possesses the highest viscosity of any glass, which is reduced with the addition of an oxide such as Y_2O_3 . Differences in intergranular glass viscosities at a given temperature may be attributed to differences in the glass compositions or to differences in crystallization behavior among the different compositions. An activation energy was also calculated from the averaged viscosity data assuming an Arrhenius dependence of viscosity on temperature. The value obtained was 631.6 ± 7.6 kJ/mol. This value is consistent with the activation energy for flow of certain silicate glasses, ≈ 600 kJ/mol [15]. The activation energy for viscous flow of the silica glass in figure 3 is ≈ 570 kJ/mol.

INTERGRANULAR GLASS VISCOSITY

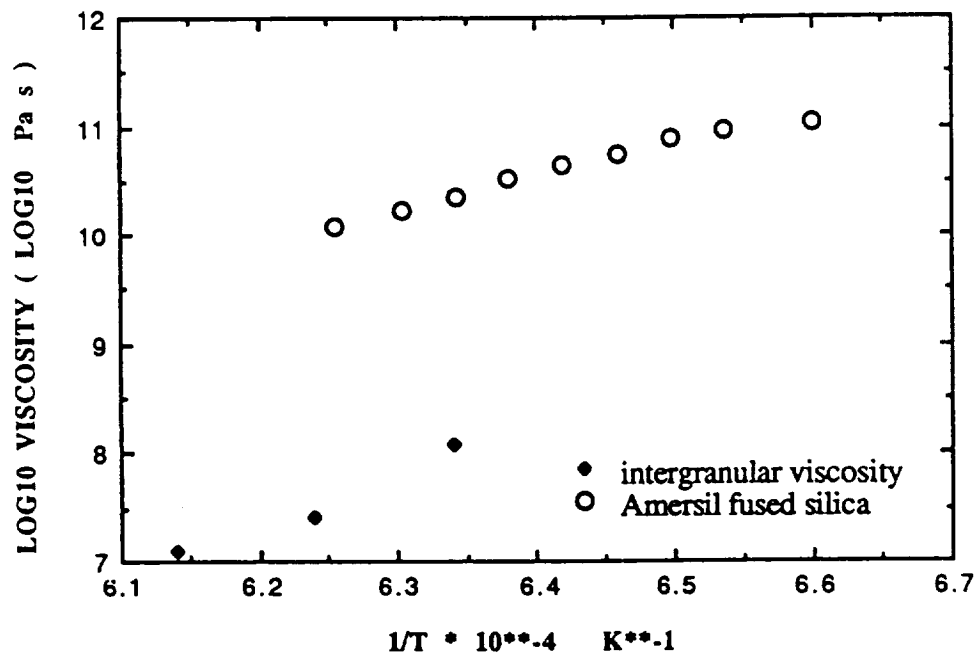


Figure 4. Sintered silicon nitride intergranular glass viscosity.

V. CONCLUSIONS

The viscosity of the intergranular glass in a yttria-sintered Si_3N_4 has been calculated from the apparent viscosity data of the bulk material. Reasonable values for intergranular glass viscosity can be obtained by using the relative viscosity values extrapolated from the physical modeling data. An activation energy for flow of the intergranular glass can be calculated from the data, and the result is comparable to the activation energy for viscous flow of certain silicate glasses.

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Crystallization of the Yttria Silicate Intergranular Phase in Silicon Nitride with Zirconia Additions

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Abstract: Crystallizing the grain boundary glassy phase in liquid-phase sintered Si_3N_4 with zirconia additions has been studied as a function of post-fabricating heat treatment. Delta- $\text{Y}_2\text{Si}_2\text{O}_7$ is crystallized in the grain boundaries after heat treatments for 2 h between 1200 C and 1400 C. Heat treatments at 1500 C and 1600 C result in the crystallization of beta- $\text{Y}_2\text{Si}_2\text{O}_7$. Details of the crystallization behavior of a simulated bulk glass composition with added zirconia is also presented.

I. Introduction

Interest in sintering covalent crystalline solids such as silicon nitride (Si_3N_4) to theoretical density stems from the potentially excellent high temperature properties which would make it suitable for applications in the aerospace industry or in gas turbine engines. In order to achieve dense silicon nitride, oxide sintering aids are generally added [1-3]. However, the glassy phase subsequently formed softens by 1200 C, degrading properties above this temperature sharply [4]. Crystallization of the intergranular phase to a more refractory phase(s) via post-sintering heat treatments is one method by which improvements in mechanical strength may be achieved [5]. The addition of zirconia to silicon nitride has proved to be an effective densifier [6,7], and is also a known nucleating agent in glass ceramics [8,9]. Previous studies [10-12] have shown Si_3N_4 with Y_2O_3 as a sintering aid to crystallize delta- $\text{Y}_2\text{Si}_2\text{O}_7$ after heat treatments for 2 h or less at 1500 C while longer heat treatments at 1500 C resulted in the crystallization of beta- $\text{Y}_2\text{Si}_2\text{O}_7$. Zirconia additions are introduced to enhance crystallization of these yttrium disilicate polymorphs, and perhaps encourage a crystallization sequence more in line with that reported by Ito and Johnson [13].

(1)

II. Experimental Procedure

The initial powders used to fabricate the simulated bulk glass composition consisted of 56.43 wt% Y_2O_3 , 38.57 wt% SiO_2 , and 5.00 wt% zyttrite. Zyttrite is a fine-particulate (0.05 micron) yttria stabilized cubic zirconia (c- ZrO_2) with 6.5 mol% Y_2O_3 . After processing and drying, the material was pressed into pellets, filled into either W or Mo crucibles, and melted at 2100 C for 4 h at either 1 or 25 atm N_2 . Annealing was performed in air at temperatures ranging from 1300 C - 1650 C at 0.5 to 120 h. The heating rate from room temperature to 1500 C was 10 C/min and the cooling rate approximately 15 C/min.

Samples were finely ground to a powder and studied by x-ray diffraction after heat treatment. Analytical electron microscopy was performed. Standard ceramographic techniques were used in the preparation of TEM specimens. Three mm discs were cut ultrasonically and then mechanically wet polished to 100 microns in thickness. Final polishing and dimpling was accomplished sequentially with 15, 6 and 1 micron diamond compounds. Samples were cryomilled (two Ar^+ beams) to avoid transformations between crystalline and amorphous species. Milling was performed at 6 kV, 1 mA at angles ranging between 15 and 8 degrees. During the last 30 minutes of milling, the settings were decreased to 3 kV and 0.5 mA to remove amorphous layer build-up. Selected area diffraction patterns of yttrium disilicate polymorphs were solved using the computer program DFTools and crystallographic data previously reviewed by Liddel and Thompson [14].

Silicon nitride samples were prepared from initial powders: 92.44 wt% Si_3N_4 , 6.96 wt% Y_2O_3 , and 0.6 wt% zyttrite. The amount of zyttrite added approximately equaled 5 wt% in the intergranular phase. The powders were milled in high-purity silicon nitride grinding media and ethanol. They were then vacuum dried and die pressed at 21 MPa and subsequently cold isostatically pressed at 50 atm N_2 . The samples were heat treated in a nitrogen atmosphere for 2 h at temperatures ranging from 1200 C to 1600 C and at 1500 C for 5 and 20 h. The heating rate from room temperature was 42 C/min and cooling rate approximately 130 C/min upon turning off the furnaces.

X-ray diffraction was performed on solid silicon nitride samples. TEM specimen preparation was similarly performed as described above, however, samples were polished to 60 microns in thickness before dimpling and ion milling. Electron microscopy and EDS analysis were again used to examine the grain boundary phase content.

III. Results

Bulk Glass Composition

(1) As-melted samples

The as-melted samples of the simulated bulk glass composition crystallized beta- $\text{Y}_2\text{Si}_2\text{O}_7$ regardless of nitrogen partial pressure or melting crucible employed. X-ray diffraction did not indicate any amorphous content, however bright-field TEM (Figure 1) did show silica rich pockets which were determined to be amorphous by characteristic diffuse ring patterns.

(2) Heat Treatments 1300 C - 1425 C

After heat treatments in this temperature range, at times up to 20 h, beta- $\text{Y}_2\text{Si}_2\text{O}_7$ was consistently determined to be present. At longer heat treatments, 48 to 120 h, gamma- $\text{Y}_2\text{Si}_2\text{O}_7$ was the predominant phase at 1400 C and above.

(3) Heat Treatments 1425 C - 1600 C

Gamma- $\text{Y}_2\text{Si}_2\text{O}_7$ was favored in this temperature region for all heat treatments, with exception at very short heat treatment times. At 1500 C and up to one hour heat treatments, beta-

$Y_2Si_2O_7$ remained the major phase present. Delta- $Y_2Si_2O_7$ began to crystallize at about 1600 C for those heat treatments of 5 hours or longer.

(4) Heat Treatments at 1650 C

A mixture of gamma- and delta- $Y_2Si_2O_7$ crystallized after heat treatment at 1650 C for 20 h.

Figure 2 demonstrates schematically the x-ray diffraction results obtained for the bulk glass sample melted at 1 atm N_2 in a W crucible, designated 'GS1/5(W)'. Each letter represents the phase or phases found present after heat treatment. When it was qualitatively determined that one phase predominated over another, an ">" separates them. Traces of phase present are indicated by parentheses. The horizontal lines at 1445 C and 1535 C indicate the temperatures at which the transformations from beta to gamma and gamma to delta have been previously reported.

Analytical electron microscopy performed indicated confirmation of these findings, while the presence of cristobalite as a minor phase was also verified. Zirconia was confirmed to be cubic in structure, as was the initial zyttrite powder.

Figure 3 is a schematic representation of the phase transformations in the simulated bulk glass. These results demonstrate that the transformations are sluggish. The approximate polymorphic transformations of yttrium disilicate from beta to gamma and gamma to delta occur at 1425 C and 1600 C respectively for 20 hour heat treatments. The gamma- phase appears preferentially stabilized as compared with the reported phase stability region by Ito and Johnson.

Silicon Nitride Composition

(1) As-sintered specimen

The as-sintered specimen of the 6Y Si_3N_4 with zirconia additions demonstrated an amorphous grain boundary phase as confirmed by TEM. Figure 4 shows the general morphology of the specimen with the corresponding ring pattern obtained from the intergranular phase. Figure 5 demonstrates both bright field and dark field images of the intergranular phase, the diffuse scattering of electrons again indicating the amorphous nature of the grain boundary region. EDS analysis was performed over four regions of the intergranular phase and weight percents of oxide components were calculated to be: 53.20 wt% Y_2O_3 , 44.16 wt% SiO_2 , and 2.65 wt% ZrO_2 . These results correspond well with the composition of the simulated bulk glass composition.

(2) Heat Treatments 1200 C - 1400 C

Heat treatments for 2 h between 1200 C and 1400 C crystallized delta- $Y_2Si_2O_7$ as the grain boundary phase. The morphology of the yttrium disilicate intergranular phase was characterized by a fine-grained mottled nature as shown in Figure 6.

(3) Heat Treatments 1500 C - 1600 C

An isothermal study at 1500 C for 2, 5, and 20 hour heat treatments revealed that while the yttrium disilicate polymorph crystallized was beta-Y₂Si₂O₇ in all cases, the morphology of the phase changed with increasing heat treatment times. The intergranular beta-yttrium disilicate phase had a larger grain size and appeared interconnected in contrast to the delta-phase. At 2 h heat treatment (Figure 7), beta-Y₂Si₂O₇ appeared at a single orientation, as demonstrated by dark-field images obtained using a spot diffracted by the intergranular phase, over limited areas of the microstructure. After 5 h (shown in Figure 8) and 20 h heat treatments, the beta- phase appeared at a single orientation over 5 microns and 20 microns respectively.

IV. Discussion

Reaction Sequence

a. Bulk Glass Composition

The phases of yttrium disilicate in the GS/5 compositions followed a sequence similar to that reported by Ito and Johnson, with the exception that the alpha-Y₂Si₂O₇ polymorph was never observed. The kinetics of the transformation were sluggish in all cases, the reaction being highly dependent upon time of heat treatment, as shown below:

1500 C		(0.5 h)
1425 C	1600 C	(20 h)
beta	----- gamma	----- delta
1350 C		(120 h)

Earlier studies by Kumar and Drummond examined a composition identical to the composition studied here, except that no zirconia was added. Their study revealed that beta-yttrium disilicate was not crystallized upon quenching as it was in this case. Depending upon the cooling rate of the furnace used, either delta- or gamma-Y₂Si₂O₇ crystallized. No beta-Y₂Si₂O₇ was ever observed. The initial yttrium disilicate phase crystallized upon quenching may have affected subsequent phases formed.

b. Silicon Nitride Composition

The observed reaction sequence for the intergranular phase in the 6Y Si₃N₄ composition with 0.5 wt% zyttrite added differed from that of the bulk glass significantly. The grain boundary phase was amorphous prior to heat treatment and crystallized delta-Y₂Si₂O₇ and ultimately beta- after higher temperature heat treatments as described below:

	1200 C	1400 C	(2 h)
amorphous	----- delta	----- beta	

This reaction sequence does, however, correspond well with studies previously performed on a similar 6Y composition without zirconia performed by Hilmas and Lee. In their study, the grain boundary phase was also amorphous before heat-treatment, and

similarly crystallized delta-yttrium disilicate after heat treatments at 1200 C, 2 h. However, in their study the crystallization of beta- occurred at a higher temperature, 1500 C, after heat treatments of 5 h or longer.

V. Conclusions

The introduction of zirconia to the 6Y silicon nitride composition acted to increase the number of heterogeneous sites for nucleation to accelerate the delta to beta transformation. The zirconia appears to have stabilized the presence of the beta- $\text{Y}_2\text{Si}_2\text{O}_7$ polymorph in both the GS bulk glass composition and the 6Y silicon nitride composition.

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